Pressure-Induced Antiferroquadrupole Order in CeTe

Yasuharu Kawarasaki[1], Takeshi Matsumura[1,2], Masafumi Sera[1,2], and Akira Ochiai[3]

[1] *Department of Quantum Matter, AdSM, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8530*
[2] *Institute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8530*
[3] *Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8578*

We have discovered that the magnetic phase diagram of CeTe under high pressure becomes quite similar to that of CeB_6, strongly suggesting that an antiferroquadrupolar ordering is realized. At 1.2 GPa, the transition temperature increases from 3 K at 0.5 T to 6.3 K at 14.5 T. Since the crystal-field ground state of CeTe is the Γ_7 doublet without a quadrupolar degree of freedom, this ordering is considered to be realized through the off-diagonal matrix element between Γ_7 and Γ_8 excited state, whose energy level is lowered with increasing the pressure.

Journal Ref: J. Phys. Soc. Jpn., **80**, 023713 (2011).
http://dx.doi.org/10.1143/JPSJ.80.023713

KEYWORDS: antiferroquadrupole order, magnetic phase diagram, Kondo effect, high pressure, CeTe

Hybridization between localized $4f$ and itinerant electrons causes various kinds of intriguing phenomena. One important effect of hybridization is the Kondo effect, the screening of the localized magnetic moment by the conduction electrons. The hybridization also causes magnetic interaction of Ruderman-Kittel-Kasuya-Yosida type, usually giving rise to an antiferromagnetic order. The competition between these two effects have been one of the main subjects in the field of f-electron magnetism.[1)] For fundamental understanding of the phenomena, studying physical properties of compounds with simple and well characterized electronic structure is of significant importance. Ce monochalcogenides, CeX_c (X_c=S, Se, Te), are the typical systems of such importance.

CeX_c crystallizes in a NaCl-type structure with the valence states of X_c^{2-} and Ce^{3+}. Two electrons from Ce are used to occupy the valence p-bands of X_c and one remaining electron enters into the conduction bands composed of the $5d$ orbitals of Ce. As a result, all the CeX_c's become metals with one conduction electron per formula unit. The top of the p band is at the Γ-point of the Brillouin zone, the bottom of the $5d$ band at the X-point, and the $4f$ level lies in the energy gap between the p band and the $5d$ band. All of these characters have been well established by the angle resolved photoemission spectroscopy and the de Haas-van Alphen effect measurement.[2,3)]

One of the unsolved problems in the CeX_c system is the small ordered moment in CeTe. All the three compounds exhibit type-II antiferromagnetic (AFM) orders with $\boldsymbol{q}=\frac{\pi}{a}(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ at T_N=2.2 K for CeTe, 5.4 K for CeSe, and 8.4 K for CeS.[4–7)] The ordered moment at the lowest temperature is 0.3 μ_B for CeTe, 0.56 μ_B for CeSe, and 0.57 μ_B for CeS. It is well established that the crystalline electric field (CEF) ground state is the Γ_7 doublet and the Γ_8 quartet excited state is located at 32 K for CeTe, 116 K for CeSe, and 140 K for CeS.[6–8)] The reductions of the ordered moment from 0.71 μ_B expected for Γ_7 may be due to the Kondo effect. However, contrary to the sequence of the moment reduction, the hybridization effect is considered the strongest in CeS and the weakest in CeTe, which is inferred from the sequence of the lattice constant and the Néel temperature. CeX_c system is considered to be located in the low hybridization regime in the Doniach's diagram. This interpretation is actually supported by the change in the spectral width of the CEF excitation in neutron scattering; CeS has the broadest width and CeTe the narrowest.[9)] Although a possibility of ferromagnetic correlation is theoretically suggested to be in competition with the AFM order, no such indication has been observed experimentally.[10)]

In order to study the hybridization effect in CeTe, we have performed magnetization measurements under high pressure. By examining the changes in T_N and the saturation moment by pressure, it is expected that more direct information on the hybridization effect can be extracted than by comparing the properties among different chalcogen compounds. Exceeding what we expected from the above motivation, we have discovered that the field-induced phase at an ambient pressure becomes dominant under high pressure. Although this phase was suggested to be associated with an antiferroquadrupole (AFQ) order, it remained uncertain and no detailed study has been performed.[3)] In this Letter, we report on the unexpected expansion of this ordered phase, which is quite likely to be an AFQ order similar to that of CeB_6.

The magnetization measurement was performed by a standard extraction method using a 15 T cryomagnet system and also by using a SQUID magnetometer (Quantum Design, MPMS, up to 5 T). We used CuBe based piston-cylinder type high pressure clamp-cells with outer diameters of 16 mm and 8.7 mm for the measurements in the 15 T magnet and the SQUID magnetometer, respectively.[11)] Daphne oil was used as a pressure transmitting medium. Pressure at low temperature was determined by measuring the superconducting transition temperature of Sn. Details of the sample preparation are described in ref. 3. A cube shaped single crystal with (001) cleaved surfaces was put in the pressure cell and the magnetic field was applied along the [001] direction.

Figure 1 shows the temperature dependences of the

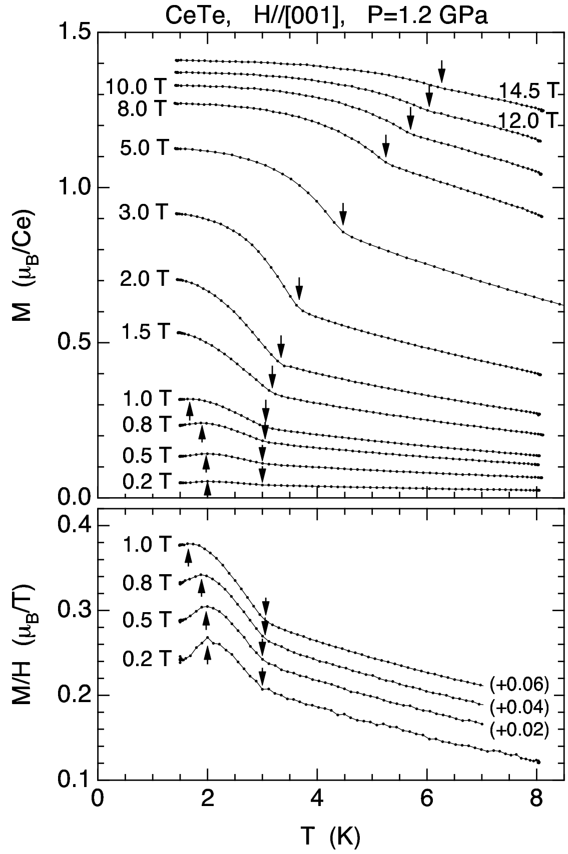

Fig. 1. Temperature dependence of magnetization under high pressure of 1.2 GPa. Arrows indicate the transition temperatures. Low field region is shown in the bottom figure in the form of M/H with vertical shifts indicated in the parentheses.

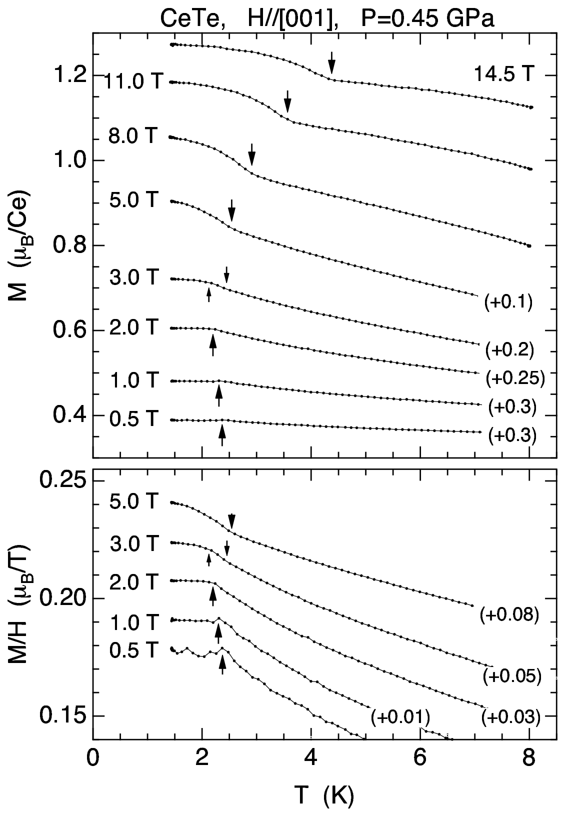

Fig. 2. Temperature dependence of magnetization under high pressure of 0.45 GPa. Arrows indicate the transition temperatures. Low field region is shown in the bottom figure in the form of M/H with vertical shifts indicated in the parentheses.

magnetization at 1.2 GPa, the maximum pressure in the present study, measured in the 15 T magnet. At low fields below 1 T, two anomalies are clearly observed, indicating phase transitions. One is at around 3 K, below which $M(T)$ exhibits an upturn. The other is at around 2 K, where $M(T)$ exhibits a cusp. The temperatures for the former and the latter transitions were determined by taking the second and the first derivatives of the $M(T)$ curve, respectively, which are indicated by the arrows in the figure. The anomaly at 2 K is considered as reflecting an AFM order. The transition temperature decreases with increasing the field. On the other hand, the temperature for the 3 K anomaly at 0.2 T increases with increasing the field and reaches 6.3 K at 14.5 T. This behavior is hardly expected from normal antiferromagnetic orderings.

This anomalous behavior of $M(T)$ in Fig. 1 immediately reminds us that of CeB_6, a typical system exhibiting an AFQ and AFM orderings with $T_Q = 3.3$ K and $T_N = 2.3$ K, respectively. The upturn in $M(T)$ on entering the AFQ phase and the increase in T_Q with increasing the field are quite similar to those of CeB_6.[12–14] This close resemblance strongly suggests an AFQ order in CeTe at 1.2 GPa.

Figure 2 shows the results at 0.45 GPa measured also in the 15 T magnet. At low fields below 3 T, only the anomaly corresponding to the AFM order is observed. The anomaly corresponding to the AFQ order is observed clearly only above 5 T. At 3 T, it was difficult to determine the transition temperatures unambiguously because the anomalies in $M(T)$ were very weak. The small arrows in Fig. 2 indicate the weak anomalies which we consider as the AFQ and AFM orderings from the characteristics of the temperature derivatives.

The experimentally determined transition points are summarized in the H-T magnetic phase diagram in Fig. 3.[15] The ordered phases are numbered I and II after ref. 3. The AFM phase at 1.2 GPa is numbered I' because it is not certain whether its magnetic structure is the same as that of phase I. The phase I is connected to the paramagnetic phase, whereas the phase I' is inside the phase II, suggesting that the I-II and the I'-II transitions are first and second order, respectively. Experimental data indicating the boundary between phases I and II for 0 GPa and 0.45 GPa are shown in Fig. 4. The first derivative of the $M(H)$ curve exhibits a clear peak when crossing the boundary between phases I and II, referred to as $H_c^{\text{I-II}}$ hereafter.

The Néel temperature initially increases with increasing the pressure. T_N at 0.5 T is 2.0 K at 0 GPa, whereas it increases to 2.35 K at 0.45 GPa. $H_c^{\text{I-II}}$ also increases linearly from 1 T at 0 GPa to 4 T at 0.45 GPa. These results imply that the antiferromagnetic interaction is enhanced by the pressure through an increase in the hybridization, which is consistent with the initial conjecture

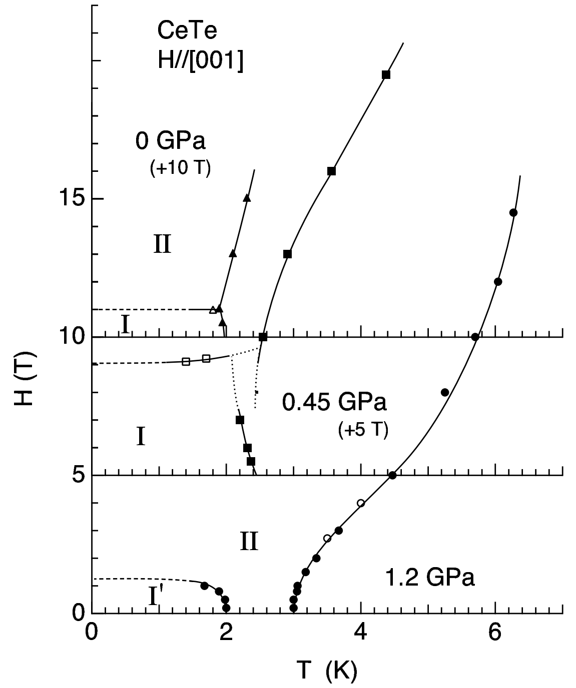

Fig. 3. Magnetic phase diagram of CeTe under high pressures. Solid and open symbols are from $M(T)$ and $M(H)$ measurements, respectively. The vertical axes for 0 GPa and 0.45 GPa are shifted by 10 T and 5 T, respectively. The lines are guides for the eye. The dashed lines are speculations to T=0. The dotted lines for 0.45 GPa are the obscure boundaries that were difficult to determine unambiguously.

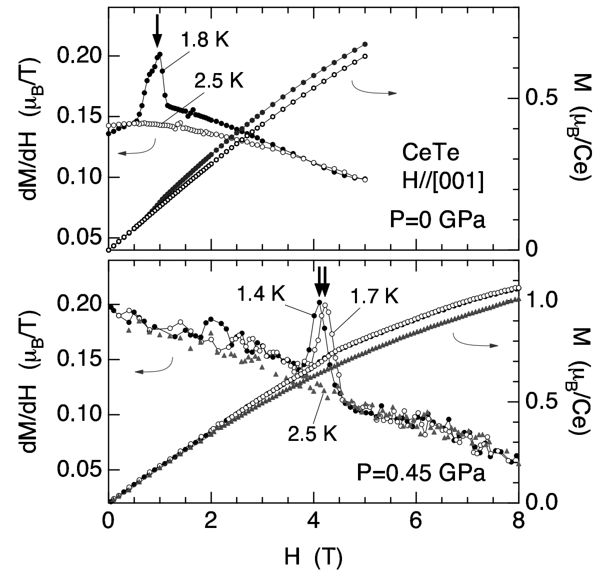

Fig. 4. Magnetic-field dependences of magnetization and their field derivatives. The $M(H)$ curves were measured in the SQUID magnetometer for P=0 GPa and in the 15 T magnet for P=0.45 GPa, respectively. The arrows on the peaks in dM/dH represent the phase boundaries plotted in Fig. 3.

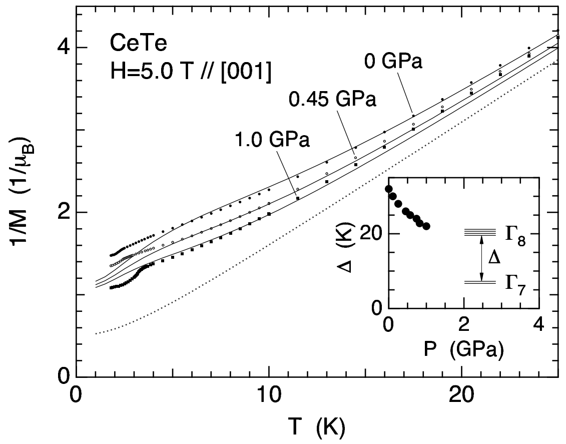

Fig. 5. Temperature dependences of inverse magnetization at H=5 T. The solid lines are the calculated curves described in the text. The dotted line is for a free ion without CEF. The inset shows the pressure dependence of the CEF splitting obtained from the fitting.

that the $\mathrm{CeX_c}$ system is located in the low hybridization regime in the Doniach's diagram. It is intriguing that the increase in $H_c^{\text{I-II}}$ is much larger than the increase in T_N.

Above 0.5 GPa, the AFQ interaction seems to overcome the competition with the AFM interaction. One difficulty in describing this region stems from the fact that the $M(H)$ curve does not exhibit a detectable anomaly at $H_c^{\text{I-II}}$ as those in Fig. 4. Nevertheless, if we regard $H_c^{\text{I-II}}$ as the critical field above which the $M(T)$ curve exhibits the upturn anomaly at T_Q, as is the case below 0.5 GPa, it is inferred that $H_c^{\text{I-II}}$ above 0.5 GPa decreases with increasing the pressure. Although it is speculated that the phase II comes down to H=0 around 1 GPa with $T_\mathrm{Q} > T_\mathrm{N}$, no clear data has been obtained yet. Details of this crossover region will be a subject in future research.

If the phase II were really the AFQ phase, the Γ_8 excited state must be involved because the Γ_7 ground state has no quadrupolar degree of freedom. Since the phase II is more enhanced by the pressure, the Γ_8 level is expected to be lowered with increasing the pressure. One evidence is the increase in the saturation moment estimated at 14.5 T. To demonstrate the Γ_8-level lowering more clearly, we show in Fig. 5 the temperature dependences of the inverse magnetization as a function of pressure. As expected, the deviation from the free ion curve reflecting the CEF is suppressed with increasing the pressure. The splitting energy, Δ, was estimated by comparing the data with the calculated curves from $\mathcal{H} = \Delta(O_4^0 + 5O_4^4)/360 + g\mu_\mathrm{B} J_z H$, where the first term represents the CEF for a Ce^{3+} ion and the second term the Zeeman effect.[16] The obtained parameter Δ is shown in the inset. At low temperatures below 5 K, the data deviate from the calculated curve because of the inter-ionic interaction and the orderings, which are not taken into account in the calculation.

The AFQ ordering with the Γ_7 ground state has been studied previously by Hanzawa.[17] The most important point in this case is that the E_g-type quadrupolar moments, O_{20} and O_{22}, have a large diagonal matrix element between the Γ_8 states, whereas the T_{2g}-type moments, O_{yz}, O_{zx}, and O_{xy}, have a large off-diagonal matrix element between the Γ_7 and Γ_8 states. No element exists between the Γ_7. As a result, when a E_g-type quadrupolar moment orders, the Γ_8 splits into two doublets and one of them necessarily becomes the ground state, resulting in a huge level splitting which would affect the properties significantly. The ordering is simply destroyed in magnetic fields by the Zeeman splitting of the Γ_8 quartet. On the other hand, when a T_{2g}-type quadrupolar moment orders, some of the Γ_8 component is mixed into the Γ_7 ground state and the Γ_8 splits into two doublets at the excited level. When a magnetic field is applied, the ratio of the Γ_8 component in the ground state increases, the order parameter is enhanced through the off-diagonal matrix element, and the transition temperature increases. This is consistent with the present experimental results. Therefore, the AFQ order parameter in CeTe under high pressure is likely to be of T_{2g}-type. The calculated magnetic phase diagram and the $M(T)$ curves for the O_{yz}-type order parameter seems to reproduce the present experimental result very well.[17)]

The suppression of the CEF by the pressure is also intriguing because this is associated with the hybridization and the Coulomb interactions with the itinerant p and d electrons. It should be noted that this is also observed in Ce monopnictides.[18,19)] The point charge effect has nothing to do with this phenomenon because the volume compression should lead to the increase in the CEF. In addition, the volume compression is about 1.7 % at 1 GPa,[20)] which corresponds to the reduction in the interionic distance by about 0.57 %, giving negligibly smaller change in the point charge effect than the observation shown in Fig. 5.

The existence of the p-f mixing in CeTe has been evidenced by the angle resolved photoemission spectroscopy.[2)] With respect to the contribution of the p-f mixing to the CEF, previous theoretical study for Ce monopnictides may be applied.[21)] In contrast to Ce monopnictides, it is not necessary to consider the $f \rightarrow p$ transfer process (f^0 intermediate state) because the valence p-band is fully occupied in CeX_c. Only the $p \rightarrow f$ transfer process (f^2 intermediate state) contributes to the shift of the CEF level. Fig. 2 of ref. 21 shows that this process favors the Γ_7 to be the ground state. If we ascribe the Γ_8-level lowering to this p-f mixing effect, the lowering corresponds to the increase in the transfer parameter $(pf\pi)/(pf\sigma)$. However, it seems unreasonable to assume $(pf\pi)$ increases more than $(pf\sigma)$ under pressure.

The change in the CEF under pressure is considered to be associated with the change in the d-f Coulomb and hybridization effects. However, a quantitative argument is quite difficult. Since the occupied $5d$ conduction band mainly consists of the t_{2g} orbitals, the d-f direct Coulomb interaction favors the Γ_8 to be the ground state to avoid the Coulomb repulsion energy. On the other hand, the d-f exchange Coulomb interaction favors the opposite.[21,22)] It is also argued that the d-f hybridization effect plays a major role.[10,23)]

In summary, we have found that the field-induced phase II of CeTe at ambient pressure is stabilized under high pressure. From the close resemblance of the magnetic phase diagram with that of CeB_6, this phase is almost certainly an AFQ ordered phase, which was suggested previously but was uncertain.[3)] This AFQ order is considered to be caused by the off-diagonal matrix element of O_{yz}, O_{zx}, and O_{xy} between the Γ_7 ground state and the Γ_8 excited state. Magnetization measurements for other field directions to study the anisotropy are in progress. To prove the AFQ order, microscopic investigation of a field induced antiferromagnetism by neutron diffraction or NMR is necessary. The moment reduction at ambient pressure might be associated with the competition with the AFQ order, but it is still an open question. It was also shown that the Γ_8 energy level is lowered down by the pressure, which is probably associated with the d-f Coulomb and hybridization effects. We consider that the Γ_8-level lowering stabilizes the AFQ order. Studies in more higher pressures will be very interesting from expectations of further increase in T_Q, lowering in the Γ_8 energy level, and increase in the Kondo effect.

Acknowledgment

The authors acknowledge Dr. R. Shiina for valuable discussions. This work was supported by Grants-in-Aid for Scientific Research (No. 21244056 and No. 21102515).

1) S. Doniach: Physica B+C **91** (1977) 231.
2) M. Nakayama, H. Aoki, A. Ochiai, T. Ito, H. Kumigashira, T. Takahashi and H. Harima: Phys. Rev. B **69** (2004) 155116.
3) M. Nakayama, N. Kimura, H. Aoki, A. Ochiai, C. Terakura, T. Terashima and S. Uji: Phys. Rev. B **70** (2004) 054421.
4) F. Hulliger, B. Natterer and H. R. Ott: J. Magn. Magn. Mater. **8**(1978) 87.
5) H. R. Ott, J. K. Kjems and F. Hulliger: Phys. Rev. Lett. **42** (1979) 1378.
6) A. Dönni, A. Furrer, P. Fisher, S. M. Hayden, F. Hulliger and T. Suzuki: J. Phys: Condens. Matter **5** (1993) 1119.
7) A. Dönni, A. Furrer, P. Fisher and F. Hulliger: Physica B **186-188** (1993) 541.
8) J. Rossat-Mignod, J. M. Effantin, P. Burlet, T. Chattopadhyay, L. P. Regnault, H. Bartholin, C. Vettier, O. Vogt, D. Ravot and J. C. Achart: J. Magn. Magn. Mater. **52** (1985) 111.
9) Although the spectra for CeS and CeTe are not available in refs. 7 and 8, the widths have also been confirmed by our own measurements.
10) N. Kioussis, E. M. Collins, S. P. Lim and B. R. Cooper: Physica B **296** (2001) 210.
11) Y. Uwatoko, T. Hotta, E. Matsuoka, H. Mori, T. Ohki, J. L. Sarrao, J. D. Thompson, N. Môri and G. Oomi: Rev. High Pressure Sci. Technol. **7** (1998) 1508.
12) J. M. Effantin, J. Rossat-Mignod, P. Burlet, H. Bartholin, S. Kunii and T. Kasuya: J. Magn. Magn. Mater. **47&48** (1985) 145.
13) N. Sato, S. Kunii, I. Oguro, T. Komatsubara and T. Kasuya: J. Phys. Soc. Jpn. **53** (1984) 3967.
14) T. Tayama, T. Sakakibara, K. Tenya, H. Amitsuka and S. Kunii: J. Phys. Soc. Jpn. **66** (1997) 2268.
15) The diagram for 0 GPa was obtained in the present study. It is basically the same as that of ref. 3. However, the jumps in the 0.5 T, 1 T, and 3 T data in Fig. 4 of ref. 3 were not observed. This is probably due to a sample dependence that become more prominent near the phase boundary at 1 T.
16) K. R. Lea, M. J. M. Leask and W. P. Wolf: J. Phys. Chem. Solids **23** (1962) 1381.
17) K. Hanzawa and T. Kasuya: J. Phys. Soc. Jpn. **53** (1984) 1809.
18) M. Kohgi, T. Osakabe, N. Môri, H. Takahashi, Y. Okayama, H. Yoshizawa, Y. Ohara, S. Ikeda, T. Suzuki and Y. Haga: Physica B **186-188** (1993) 393.
19) H. Yoshizawa, Y. Okayama, Y. Oohara, H. Takahashi, N. Môri, S. Mitsuda, T. Osakabe, M. Kohgi, Y. Haga and T. Suzuki: J. Phys. Soc. Jpn. **64** (1995) 617.

20) J. M. Leger, R. Epain, J. Loriers, D. Ravot and J. Rossat-Mignod: Phys. Rev. B **28** (1983) 7125.
21) H. Takahashi and T. Kasuya: J. Phys. C: Solid State Phys. **18** (1985) 2709.
22) D. Schmitt: Journal of Physics F: Metal Physics **9** (1979) 1745.
23) J. M. Wills and B. R. Cooper: Phys. Rev. B **36** (1987) 3809.